Controlled Macromolecular Synthesis from a Novel Polymerization Process

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Introduction

Reaction control in polymerizing systems is often undermined by the presence of external agents like surfactants [1], metallic complexes [2], or copper [3]. Since the controlling mechanism depends on chemical mediation, spatially directed reaction control from such systems in micro- and nanoscale dimensions is not possible. Recent advances [4] in chemical synthesis by using an atomic force microscope (AFM) are directed toward such control aspects in nanoscale dimensions. Such nanostructures are of great interest in areas such as drug delivery systems, optical barriers, resists, packaging materials, and encapsulation of semiconductors. In the current work, we discuss a novel polymerization process to control the reaction *in situ*, directly resulting in polymeric nanoparticles and in spatially directed polymer patterns.

Methods and Materials

The controlling chemistry of this so-called free-radical retrograde precipitation polymerization process (FRRPP) [5] is based on the free-radical reaction in the retrograde phase envelope of a polymer-monomer-solvent system. The exotherm of the polymerization reaction induces local "hot spots," pushing the reactive domains deeper into the phase envelope and precipitating the growing polymer chains. This results in reduced propagation and termination rates, which lead to narrow molecular weight distributions and trapped "live radicals." This reaction, when carried out in a quiescent fluid, will limit itself to the growing polymer domains, resulting in polymeric nanoparticles [6]. Hence, we proceeded to investigate the growing polymer domains *in situ*. Showing that there is a persistent existence of nanoparticles, we further went on to investigate the spatial reaction control aspects of this process (Fig. 1).

The kinetics of FRRPP of methacrylic acid in water was studied previously in our group [7]. Dynamic small-angle x-ray scattering (SAXS) analysis of methacrylic acid was carried out at the Basic Energy Sciences Synchrotron Radiation Center Collaborative Access Team (BESSRC-CAT) beamline, sector 11 of the APS. Polymerization was monitored by placing the sample in the holder while simultaneously gathering the SAXS data
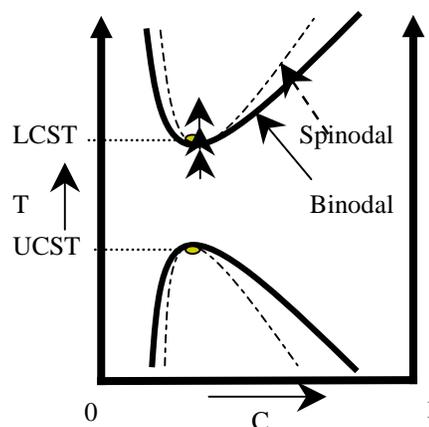
FIG. 1. *Phase diagram of a polymer-solvent system, given as temperature vs. concentration. Both the upper critical solution temperature (UCST) and lower critical solution temperature (LCST) are shown.*

for a set reaction time of 30 min. The reaction was carried out at two different temperatures, 60° and 80°C. To validate the persistence of size from kinetic experiments, SAXS data from pre-reacted samples were also obtained. The same reaction recipe [7] was used to react the samples before they underwent freeze-thaw cycles and flame sealing. These pre-reacted samples were then placed in the sample-holder maintained at reaction temperature to observe the particle behavior in a simulated reaction environment.

Spatially directed radiation initiation studies were carried out at APS Synchrotron Radiation Instrumentation (SRI)-CAT beamline 2-BM. N-isopropylacrylamide (NIPAM) in water was previously studied as an FRRPP reaction recipe [8]. In the current study, a similar recipe was prepared with 20% NIPAM in water. Calcium methacrylate was added as a cross-linker at 10% (wt/wt) with respect to the monomer. A thin film of this mixture was captured between two oxidized silicon wafers. The wafer assembly was then sealed and exposed to hard x-rays. A grid pattern through which hard x-rays were incident upon the wafer assembly was used to verify the hypothesis of size confinement. A dosage of 500 J/cm^3

was applied, and immediately after this, the reaction was stopped by freezing the wafer assembly in dry ice. The resulting polymer pattern was developed by dismantling the wafer assembly and washing it with water.

Results

The *in situ* SAXS analysis from the (1) reactive systems at 60°C, (2) reactive systems at 80°C, and (3) pre-reacted system resulted in data that fit the Debye function for flexible polymer chains through the range of low-q with good accuracy. The radius of gyration R_g thus obtained from the data fits is given in Table 1.

Table 1. Radius of gyration obtained from the SAXS data fits for the different FRRPP systems.

Methacrylic acid/ water system	R_g (Å) after time (in min) below		
	1.5	15	30
Reacting at 60°C	59	54	53
Reacting at 80°C	111	139	118
Pre-reacted for 15 min at 60°C	126	100	97

An optical microscope image of the observed polymer pattern is shown in Fig. 2. The polymer product formed a grid. The unreacted monomer solution was washed away with water after the wafer assembly was frozen. Note the sharp change at the interface of the polymer grid and the neighboring regions. Although the monomers are throughout the wafer surface, the reaction has not propagated to neighboring molecules but confined itself only to the irradiated regions of the film. A closer look indicates that the radiation cross section generated a high crosslink material that is 25-µm thick. A lower crosslink material 10-20 µm away from the high crosslink core was produced.

Discussion

Since the polymer is in a retrograde precipitating environment, in the absence of a reaction, we would expect it to shrink in size as we observe its behavior over a period of time. This is particularly true for the case of the pre-reacted system, whose average R_g shrank from 126 to 97 Å. The reactive system is not as simple to predict. The reaction kinetics influence factors such as the molecular weight and local temperature of the reaction
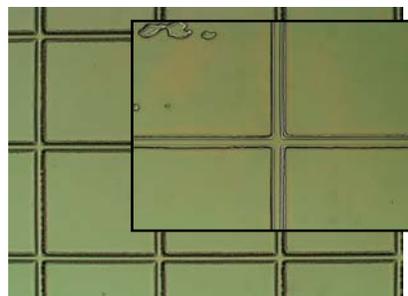
FIG. 2. An optical microscope image of the matrix polymer pattern developed in situ. A zoomed-in image of the cross lines points out the lack of reaction spread to the reactive fluid around it.

domain, which will have a contradictory effect on the size of the polymer. As the reaction proceeds in a domain, the molecular weight increases, and, with that, one would normally expect an increase in the size of the polymer. Since the reaction is exothermic, the increase in molecular weight also results in an increase in temperature, causing more shrinkage. This, however, is a highly simplified model of the reaction environment. More complications arise as the temperature gets higher and higher, which can be explained in light of polydispersity data. The radius-of-gyration data from the reaction at 60°C suggest that the particles have proceeded along the lines as explained above. Nevertheless, the data from the reaction at 80°C do not follow a similar pattern. Although it is not surprising, it would be interesting to look into the factors influencing particle growth at that temperature. The study of polymerization reaction *in situ* through SAXS would therefore give us an insight into the formation of nanostructures. This understanding could later be used to determine the possibility of fine structure patterning from various recipes and operating conditions.

It was shown that the reaction control observed in FRRPP could be translated into dimensional control, depending on the reactor system and type of initiation. Nanoparticles could be obtained from the monomer under precipitating conditions above the LCST. On one hand, in a well-mixed fluid, particle-particle agglomeration and polymer chain collapse would result in only a few surviving nanoparticles. On the other hand, in a quiescent system, unagglomerated nanoparticles were obtained. Excellent reaction control was observed when the reaction was selectively initiated with radiation. Future work should thus be directed toward understanding the controlling parameters in the selective initiation of reactive domains. The procedure needs to be optimized with respect to the reaction recipe and the overall dosage. This could be done by incorporating a radical scavenger in the recipe in order to minimize the formation of

lower-crosslink-density material around the high-crosslink core, which seemed to be coincident with the radiation cross section.

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